

Ambient concentrations of PM₁₀, PM₁₀-bound polycyclic aromatic hydrocarbons and heavy metals in an urban site of Győr, Hungary

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Abstract An assessment of the air quality of Győr (Hungary) was performed by determining the ambient concentrations of PM₁₀, PM₁₀-bound polycyclic aromatic hydrocarbons (PAHs) and regulated heavy metals (Pb, Cd, As and Ni) in the period of 2008–2012. The PM₁₀ concentrations ranged from 7.90 to 119.14 µg/m³ with the mean value of 34.94 µg/m³. On average, the total PAHs (sum of the concentrations of 18 individual PAH compounds) and the four metals contents in the PM₁₀ fraction amounted to 0.04 and 0.06 %, respectively. The total PAH concentrations ranged from 0.29 to 88.30 ng/m³, which were predominated by intermediate and high molecular weight PAHs. Higher concentrations of both PM₁₀ and PAHs were detected in samples collected in the heating seasons. The mean metallic concentrations calculated for the 5-year sampling period were found in decreasing order of Pb (14.47 ng/m³), Ni (3.73 ng/m³), As (0.64 ng/m³) and Cd (0.60 ng/m³). Very little seasonal variation was observed in metal concentrations. Moreover, the comparison of the PM₁₀, benzo[*a*]pyrene (BaP) and heavy metal concentrations determined with other Hungarian and European urban sites and the limit or target values for health protection has revealed that the air quality of Győr and other Hungarian cities for the above pollutants generally corresponds to the EU average. It is important to reduce PM₁₀ and BaP pollution to concentrations lower than those specified in current legislation. However, the Hungarian cities have excellent air quality with respect to heavy metals.

Keywords Air quality · PM₁₀ · PAH · Heavy metal · Monitoring

Introduction

Airborne particulate matter (PM) is one of the most important environmental pollutants in terms of adverse effects on human health (WHO 2000, 2005; EEA 2013). It consists of a complex mixture of solid and liquid particles of organic and inorganic substances suspended in the air. PM is thought to contribute to cardiovascular and cerebrovascular disease by the mechanisms of systemic inflammation, direct and indirect coagulation activation and direct translocation into systemic circulation (Grahame and Schlesinger 2010; Araujo 2011; Breysee et al. 2013). Respiratory diseases are also exacerbated by exposure to PM. PM causes respiratory morbidity and mortality by creating oxidative stress and inflammation that leads to pulmonary anatomic and physiologic remodelling (Anderson et al. 2012; Mehta et al. 2013). Epidemiological studies have established linkage between the concentration/composition of the inhalable (particle size <10 µm) and respirable (particle size <2.5 µm) fractions and adverse respiratory health effects. Because of the particular interest, these fractions are designated as PM₁₀ and PM_{2.5}, respectively. Their chemical and physical compositions vary depending on location, emission sources and atmospheric and weather conditions (WHO 2005; Rodríguez et al. 2007; Ravindra et al. 2008a; EEA 2013).

One of the organic groups in PM in terms of health risk is polycyclic aromatic hydrocarbons (PAHs), which have received increased attention in studies on air pollution recently because some of them are highly carcinogenic or mutagenic (WHO 2000; Saraga et al. 2010; Sram et al. 2011; Burkart

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et al. 2013). The human health risk associated to PAHs and their derivatives is higher in the urban atmospheres, considering the density of population, increasing vehicular traffic and scarce dispersion of the atmospheric pollutants. PAHs are semivolatile species formed through the fusion of two or more benzene rings by a pyrolytic process during the incomplete combustion of carbonaceous materials. PAHs can also be derived from petrogenic and diagenetic origins. Sources of PAHs in urban atmosphere include automobiles, resuspended soils, refineries and power plants (ATSDR 1995; Srogi 2007). Additional contributions to ambient air levels arise from tobacco smoking, heating sources and road dust. Possible PAH sources in road dust include diesel vehicle exhaust, gasoline vehicle exhaust, tire, pavement (asphalt or bitumen) and oil spill. Natural sources such as forest fires and volcanic eruptions are less important. PAHs are transported through the atmosphere over long distances entering other environmental media by wet and dry deposition (aerosol+gas phase) (Manoli and Samara 1999). The US Environmental Protection Agency (EPA) has identified 16 unsubstituted PAHs as priority pollutants for measurement in environmental samples. The US EPA PAHs are commonly classified into one of three groups based on their molecular structure. Low molecular weight (LMW) PAHs have two or three aromatic rings, intermediate molecular weight (MMW) PAHs have four rings, while high molecular weight (HMW) PAHs have five or six rings. Differences in the structure and size of individual PAHs result in substantial variability in the physical and chemical properties of these substances. One of the best characterised and most toxic PAH compound is benzo[*a*]pyrene (BaP), which is generally used as the indicator PAH (ATSDR 1995; WHO 2000; Staniszewska et al. 2013; EEA 2013).

Although metal-bearing aerosols constitute a small fraction of the PM mass, the exceeding concentration and/or long-term exposure to metals could cause severe toxic effects on human health. Moreover, they still contribute to the deposition and build-up of heavy metal contents in soils, sediments and organisms (EEA 2013). Combustion of fossil fuels and wood, exhaust emission from vehicles, industrial activities, energy production, construction and waste incineration are known to be anthropogenic sources, while volcanic activity, wind-eroded soil dusts, forest fires and sea salt spray may contribute to natural metal-bearing aerosols (WHO 2000). Many recent studies have presented that non-exhaust PM emissions from road traffic (brake and tire wear, road dust and road surface wear) have been identified as an important source of metals in the urban environment and, at locations influenced by traffic, can be more important than industrial emissions (Thorpe and Harrison 2008; Pastuszka et al. 2010). Other potential sources include clutch and engine wears, abrasion of wheel bearings, corrosion of other vehicle components, street furniture and crash barriers (Barlow et al. 2007). Some selected heavy metals such as Pb, Cd, As and Ni belong to the most

monitored and regulated pollutants in air quality (EEA 2013). The metalloid arsenic is regularly added to the list of heavy metals, based on its toxicity. Arsenic exposure is associated with increased risk of skin and lung cancer (ATSDR 2007a). Several reports show that Pb induces severe neurological and hematological effects on the exposed population especially children (ATSDR 2007b). Cadmium is associated with kidney and bone damage and has also been identified as a potential human carcinogen, causing lung cancer (ATSDR 2008). Nickel is a known carcinogen and also has other non-cancerous effects, for example on the endocrine system (ATSDR 2005).

Air monitoring stations in Hungary are operated by the Environmental Inspectorates. Within the framework of the Hungarian PM₁₀ Monitoring Programme, the PM₁₀ samples that are analysed for PAHs and heavy metals are collected on a 24-h basis, for 2 weeks in four periods a year. A part of the measured data is registered in the European air quality database maintained by the European Environment Agency (EEA). The Hungarian Meteorological Service (HMS) has reported the most important concentration data (only annual average and maximum values) of PM₁₀, regulated heavy metals (Pb, Cd, As and Ni) and BaP determined at different stations (HMS 2009, 2010, 2011, 2012, 2013). Some concentration data for other carcinogenic PAH compounds (benzo[*a*]anthracene (BaA), sum of three benzofluoranthene isomers (BbkjF), indeno[123-*cd*]pyrene (IND) and dibenzo[*ah*]anthracene (DahA)) have also been reported. However, other priority US EPA PAH compounds are not included in the HMS air quality database.

The aim of this work was to give an overview about the concentration levels of PM₁₀ as well as associated PAHs (16 US EPA PAHs, 2-methylnaphthalene (mNAP) and benzo[*j*]fluoranthene (BjF)) and regulated heavy metals (Pb, Cd, As and Ni) in an urban site of Győr (Hungary) in the period of 2008–2012. This is the first time to comprehensively study the above monitoring results of Győr. Győr is the most important city in northwest Hungary, and one of the seven main regional centres of the country. The monitoring station is under the North Transdanubian Regional Environmental Protection and Nature Conservation Inspectorate Laboratory, designated by the National PM₁₀ Monitoring Programme. The levels of pollutants determined in our study were compared with air quality standards and with published data of other Hungarian urban sites.

Materials and methods

Study area and sampling

Győr is located halfway between Wien, Bratislava, and Budapest in Central Europe. The geographical location of city

is 47°41'02" N, 17°38'06" E and has an urban population of 130,000. The location of Győr is shown in Fig. 1. The climate of Győr is continental characterised by 10.23 °C annual average temperature and 595 mm annual total precipitation. Győr is a dynamically developing city due to its good geographic location and as an emphasised centre in automotive industry. It has become one of the largest economic, industrial and traffic areas of Hungary. The monitoring station is located at the junction of Tihanyi Street and Ifjúság Boulevard, approximately 3 km south of the city centre. It can be classified as an urban traffic station.

A total of 280 PM₁₀ aerosol samples were collected at the monitoring station of Győr in the period of 2008–2012. The number of 24-h sampling days was 14 in every February, May, August and November. A Digitel High Volume sampler DHA-80 (Digitel Elektronik AG, Switzerland) was used for the collection of ambient aerosol particles, which were chemically analysed later. This equipment is considered to be equivalent to the requirements of the European Standard for sampling PM₁₀ matter (MSZ EN 12341:2000). Samples were taken onto high-purity Advantec QR-100 quartz fibre filters (size, 150 mm diameter) for a period of 24 h at a flow rate of 30 m³/h. The sampler was loaded with 14 filters, which were changed automatically every 24 h. About 720 m³ of air was pumped through a filter from midnight to midnight.

Gravimetric analysis

Before and after sampling, the filters were conditioned for 48 h at 20±1 °C and 50±5 % relative humidity. The particle total mass was determined by weighing of the sampling filters before and after sampling using a microanalytical balance (precision of 0.01 mg) and the PM₁₀ concentration calculated from the weighed mass on the filter and the sampling volume. After the sampling, the filters were wrapped in aluminium foil separately and stored in a refrigerator at 4 °C until chemical analysis.

Fig. 1 Schematic map of Hungary showing the location of Győr. Selected Hungarian air monitoring stations are also marked, the concentration data of which are included in this study



Extraction and analysis of PAHs

The 16 PAHs identified by the US EPA as priority pollutants as well as the mNAP and B_jF (listed in Table 1) were determined. The PAH analysis was conducted in accordance with the Hungarian standard method procedure (MSZ EN 15549:2008). One half of the filter was cut by a ceramic scissor, and the sample was extracted by ultrasonic liquid–solid extraction with 30 mL *n*-hexane three times. Two hundred and fifty nanograms of SV Internal Standard Mix (cat. no. 31206, Restek, Bellefonte, PA, USA) containing six deuterated surrogates (concentration, 10 µg/mL and volume, 25 µL) was added to the sample before the extraction procedure. The extract was concentrated to 1 mL by a rotary evaporator. The PAH compounds in the concentrated extract were fractionated by a silica gel column (5 g silica gel per column). The column was first eluted with 30 mL of *n*-hexane, and the eluate was discarded. Further elution was carried out with 30 mL of dichloromethane to obtain the PAH fraction. The fraction containing the PAHs was concentrated to 1 mL by using a rotary evaporator, then 100 ng of internal injection standard (cat. no. 442725, Supelco, Sigma-Aldrich Ltd., Budapest, Hungary) containing octachloro-naphthalene (concentration, 10 µg/mL and volume, 10 µL) was added to the sample for injection control.

A gas chromatography–mass selective detector (GC-MSD) system consisting of an Agilent 6890 GC (Palo Alto, CA, USA) with an Rtx-5MS Integra GC column (30 m long, 0.25 mm internal diameter, 0.25 µm coating, 5 % diphenyl–95 % dimethyl polysiloxane; Restek Bellefonte, PA, USA) and an Agilent 5973 MSD was used in the study. Helium was used as the carrier gas, and the flow rate was maintained at 1.4 mL/min (linear velocity of 43 cm/s). One microlitre sample volume was injected by applying a splitless injection technique. The temperature of the GC injector port was maintained at 250 °C. The temperature of the column was

Table 1 Concentration ranges, mean values and standard deviations of PM₁₀, PM₁₀-bound PAHs and heavy metals in an urban site of Győr, Hungary, in the period of 2008–2012

Pollutant		Sampling year				
		2008	2009	2010	2011	2012
PM ₁₀ (µg/m ³)		10.05–104.06	12.95–65.47	8.77–65.89	11.00–119.14	7.90–106.30
		35.51±24.28	27.78±10.77	31.44±16.38	47.43±31.65	32.53±25.79
PAH compounds (ng/m ³)	Total rings					
Naphthalene	2	0.10–0.40	0.60–0.70	0.09–1.62	0.11–0.90	0.02–0.54
		0.24±0.06	0.42±0.19	0.58±0.52	0.35±0.21	0.15±0.13
2-Methylnaphthalene	2	ND–0.30	0.08–0.79	0.18–0.80	0.04–0.83	0.02–0.55
		0.09±0.09	0.36±0.19	0.41±0.18	0.21±0.18	0.13±0.12
Acenaphthylene	3	ND–0.02	ND–0.04	ND–0.49	ND–0.99	ND–0.38
		<0.02	0.01±0.01	0.04±0.09	0.08±0.20	0.06±0.11
Acenaphthene	3	ND–0.10	ND–0.05	ND–0.09	ND–0.13	ND–0.04
		0.01±0.02	0.01±0.02	0.02±0.03	0.01±0.02	<0.02
Fluorene	3	ND–0.20	ND–0.10	ND–0.44	ND–0.91	ND–0.89
		0.04±0.05	0.04±0.03	0.06±0.09	0.11±0.19	0.13±0.21
Phenanthrene	3	0.03–3.90	0.06–0.58	0.04–5.27	0.02–7.58	0.03–8.56
		0.72±0.82	0.20±0.12	0.67±1.14	1.06±1.98	1.47±2.55
Anthracene	3	ND–0.60	ND–0.06	ND–0.41	ND–0.80	ND–0.85
		0.09±0.14	0.01±0.02	0.04±0.09	0.09±0.17	0.13±0.24
Fluoranthene	4	0.07–10.70	0.06–1.38	0.03–9.61	0.03–17.70	0.03–13.09
		1.65±2.29	0.47±0.36	1.40±2.13	2.71±4.54	2.67±4.49
Pyrene	4	0.06–11.20	0.04–1.48	0.02–7.09	0.04–12.12	0.02–10.22
		1.65±2.35	0.47±0.40	1.15±1.61	2.16±3.23	2.13±3.42
Benzo[<i>a</i>]anthracene	4	ND–16.60	0.03–2.33	ND–3.84	0.01–6.99	ND–5.52
		1.89±3.27	0.50±0.57	0.68±0.92	1.44±2.12	1.31±1.82
Chrysene	4	ND–10.40	0.02–3.36	ND–4.23	0.02–6.72	ND–5.04
		1.67±2.38	0.78±0.89	0.86±1.07	1.33±1.77	1.36±1.75
Benzo[<i>b+k+j</i>]fluoranthene	5	ND–16.00	0.06–6.67	ND–11.48	0.06–16.39	0.07–10.54
		2.72±3.66	1.48±1.69	1.80±2.44	3.86±5.11	3.02±3.45
Benzo[<i>a</i>]pyrene	5	ND–8.00	ND–3.54	ND–3.63	0.02–6.92	0.02–5.22
		1.13±1.73	0.53±0.73	0.68±0.85	1.54±2.08	1.16±1.47
Dibenzo[<i>ah</i>]anthracene	5	ND–2.70	ND–0.28	ND–0.58	ND–0.96	ND–0.70
		0.15±0.38	0.08±0.09	0.11±0.14	0.19±0.27	0.17±0.22
Indeno[123- <i>cd</i>]pyrene	6	ND–6.80	0.02–2.04	ND–2.92	0.03–7.88	0.02–6.63
		1.12±1.57	0.62±0.60	0.62±0.72	1.68±2.35	1.64±2.04
Benzo[<i>ghi</i>]perylene	6	ND–5.00	0.01–1.56	ND–3.34	0.03–6.43	0.03–4.19
		0.85±1.14	0.52±0.51	0.61±0.70	1.34±1.84	1.04±1.21
Total PAHs		0.82–88.30	0.95–21.68	0.51–52.87	0.85–86.99	0.29–67.40
		14.03±18.92	6.50±5.72	9.73±11.77	18.19±25.28	16.57±21.69
BaPE		0.02–10.92	0.03–4.42	ND–4.78	0.03–9.55	0.03–7.13
		1.61±2.40	0.76±0.95	0.97±1.20	2.15±2.88	1.68±2.10
Heavy metals (ng/m ³)						
Pb		3.80–36.10	2.60–25.03	3.10–14.01	1.34–40.75	0.19–65.98
		19.08±7.92	11.54±4.26	9.03±2.53	12.61±8.77	20.09±20.86
Cd		0.03–3.56	0.12–1.30	0.03–1.08	0.05–1.34	0.03–9.51
		1.06±0.82	0.66±0.32	0.36±0.29	0.38±0.20	0.52±1.26
As		0.30–2.84	ND–1.88	0.22–1.16	0.24–6.64	0.24–4.72
		0.67±0.60	0.20±0.32	0.48±0.23	0.74±1.07	1.13±1.28

Table 1 (continued)

Pollutant	Sampling year				
	2008	2009	2010	2011	2012
Ni	0.19–16.52	1.40–14.67	0.90–8.51	1.03–19.53	0.36–10.18
	4.31±3.16	4.33±2.51	3.79±1.57	3.97±2.71	2.27±2.27

ND not detected

programmed from the initial 45 °C (at $t=1$ min) to 300 °C ($t=5$ min) at a rate of 8 °C/min. The mass selective detector was operated in the electron impact mode using 70 eV. Ion source temperature was 230 °C. Selected ion monitoring mode was employed for the identification and quantification of the individual PAH compounds.

Before sample analysis, standards for calibration curve were prepared from WA EPH Aromatic Hydrocarbon Standard (cat. no. 31469, Restek, Bellefonte, PA, USA) containing 18 components by volumetric dilution to obtain five concentration levels. Surrogate standard solution mentioned above was also added to the calibration standards with the same concentration as it was used for the sample analysis. The calibration curves were obtained in triplicate. Field blank determinations were used for background correction on the sampled filters. This method resulted in a limit of detection of about 0.02 ng/m³. The total PAH concentration was calculated as the sum of the concentrations of 18 PAH species for each collected sample.

Digestion and analysis of heavy metals

The concentrations of heavy metals (Pb, Cd, As, and Ni) in the PM₁₀ aerosol fraction were measured by graphite furnace atomic absorption spectroscopy (SOLAAR MQZ, Unicam Ltd., Cambridge, UK) equipped with Zeeman and deuterium background correctors, a graphite furnace GF9, and an autosampler. The other half of the filter was treated with 15 mL aqua regia and digested at temperatures up to 210 °C for 20 min using a CEM Mars 5 microwave (CEM, NC, USA). The resulting solution was filtered and diluted to 100 mL with distilled water. A 20- μ L volume of the sample was injected into the graphite tube. The sample analysis was conducted in accordance with the Hungarian standard method procedure (MSZ EN 14902:2006). The standard solutions of the heavy metals were obtained from Merck KGaA, Darmstadt, Germany. Solutions of different concentrations were prepared by dilution of standard solutions. The limit of detection in micrograms per litre was 0.1 for Cd, 0.9 for As and 0.7 for Ni or Pb. All samples were determined in triplicate, and a difference lower than 5 % was considered acceptable. The concentrations of each metal in PM₁₀ sample (ng/m³) were calculated from the measured concentration data and air volume pulled through the filter.

Results and discussion

PM₁₀ concentration trends

Table 1 presents the concentration levels of PM₁₀, PM₁₀-bound PAHs and heavy metals in the urban atmosphere of Győr in the period of 2008–2012. The EU and the Hungarian limit and target values for health protection as well as the air quality index (AQI) used in Hungary are shown in Table 2 (Hungarian Directive 2011; EEA 2013). The monthly average PM₁₀ concentrations and standard deviations during the 5-year sampling period are demonstrated in Fig. 2.

The PM₁₀ concentrations ranged from 7.90 to 119.14 μ g/m³ depending on season. Relatively higher concentrations were detected in November and February during all the years (excluding 2009) due to increased emissions from combustion in the cold season. The PM₁₀ pollution exceeded the EU and the equivalent Hungarian daily limit value of 50 μ g/m³ in 34 and 54 % of the samples collected in November and February, respectively. However, the PM₁₀ concentrations were in the range of 7.90 and 36.50 μ g/m³ (excluding two samples) in May and August, which indicate excellent or good air quality in the sampling periods without heating. The annual average concentrations of PM₁₀ were in the range of 27.78–47.43 μ g/m³. The lowest PM₁₀ annual average concentration was observed for 2009 due to the relatively low concentrations in the heating season, which refers to a milder winter. The annual EU and equivalent Hungarian limit value of 40 μ g/m³ was exceeded in 2011.

In a previous study carried out within the European Study of Cohorts for Air Pollution Effects (ESCAPE) project, PM (PM₁₀ and PM_{2.5}) samples were collected at 20 urban sites of Győr for 2 weeks in three time periods (1, winter; 2, summer; and 3, spring or autumn) between 25 February 2010 and 24 February 2011 (Vaskövi et al. 2014). The PM₁₀ concentrations ranged from 25 to 47 μ g/m³ at the traffic-related sites and from 23 to 42 μ g/m³ at the background sites with the mean values of 32 and 29 μ g/m³, respectively. The PM₁₀ levels were in the range of 40–50 μ g/m³ at only three sites in the first and third sampling periods. Nevertheless, the annual average PM₁₀ concentration of Győr calculated for the whole urban area (30.5 μ g/m³) was compared with our data (33.2 μ g/m³) determined for the same 1-year sampling period.

Table 2 EU and Hungarian air quality limit or target values of PM₁₀, PM₁₀-bound benzo[*a*]pyrene and heavy metals for health protection as well as air quality index used in Hungary (EEA 2013; Hungarian Directive 2011)

Pollutant	EU limit or target value ^a	Hungarian limit value	Quality index used in Hungary ^e				
			1. Excellent	2. Good	3. Acceptable	4. Polluted	5. Heavily polluted
PM ₁₀ (24-h mean) (μg/m ³)	50 ^b	50 ^b	0–20	20–40	40–50	50–90	90–
PM ₁₀ (annual mean) (μg/m ³)	40	40	0–16	16–32	32–40	40–80	80–
BaP (24-h mean) (ng/m ³)	–	1	0–0.4	0.4–0.8	0.8–1	1–2	2–
BaP (annual mean) (ng/m ³)	1 ^c	0.12	0–0.048	0.048–0.092	0.092–0.12	0.12–0.24	0.24–
Heavy metals (annual mean) (ng/m ³)							
Pb	500	300	0–120	120–240	240–300	300–600	600–
Cd	5 ^d	5	0–2	2–4	4–5	5–10	10–
As	6 ^d	10	0–4	4–8	8–10	10–20	20–
Ni	20 ^d	25	0–10	10–20	20–25	25–50	50–

^a EU limit values are legally binding EU parameters that must not be exceeded. Limit values are set for individual pollutants and are made up of a concentration value, an averaging time over which it is to be measured, the number of exceedences allowed per year, if any, and a date by which it must be achieved. Target values are also used in the EU and are set out in the same way as limit values. They are to be attained where possible by taking all necessary measures not entailing disproportionate costs

^b Not to be exceeded on more than 35 days/year

^c Target value to be met by 2013

^d Target value, entering into force on 31 December 2012

^e Percentage of the limit value: excellent, 0–40 %; good, 40–80 %; acceptable, 80–100 %; polluted, 100–200 %; heavily polluted, 200 % +

These results proved that the Győr monitoring station presented in our work, during this 1-year period, representatively reflected the annual level of PM₁₀ as far as the whole town is considered.

Concentration and distribution of PM₁₀-bound PAHs

All of the priority 16 US EPA PAH compounds, mNAP, and B_jF were identified in the Győr PM₁₀ samples. The total PAHs mass concentrations for the 5-year sampling period were 0.29–88.30 ng/m³, with a mean of 13 ng/m³, and on average accounted for 0.04 % of the PM₁₀ mass. The temporal distribution of total PAHs concentrations is presented in Fig. 3a. Similar to the PM₁₀ concentration trend, relatively higher PAH concentrations were detected in samples collected in November and February during all the years compared with

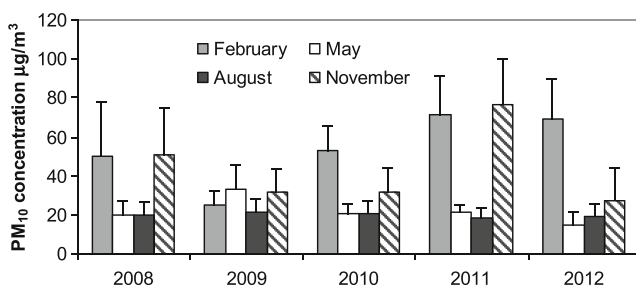


Fig. 2 Temporal variation of PM₁₀ mass concentration in Győr, Hungary (error bars represent one standard deviation)

May and August. This trend may be caused by fewer car journeys made in cities in summer and decreased residential and power station fuel combustion for heating and energy in the spring and summer months. A previous study showed that similar concentration trend of PAHs was observed in Budapest PM₁₀ samples (Muránszky et al. 2011). In addition, relatively higher PAH concentrations were detected in Budapest during winter compared with other seasons due to the more fuel combustion and heating in winter.

The compositional pattern of PAHs by aromatic rings in the urban site of Győr is shown in Fig. 4. The four-ring PAHs were the most abundant PAHs in PM₁₀ samples, which averaged 43.5 % of total PAHs. The five- and six-ring PAHs together averaged 44.1 % of total PAHs. The LMW-PAHs (two and three rings) were less present (12.4 %). B_bk_jF and fluo-ranthene (FLT) were the most dominant species followed by pyrene (PYR) and chrysene (CHR). The carcinogenic species (BaP, BaA, B_bk_jF, IND and DahA) together contributed 46.4 % of the mass of the total PAHs on average. Studying the seasonal variation of PAHs, it was found that the LMW PAHs had a higher contribution in the non-heating seasons (averaged 36.9 % of total PAHs). Naphthalene, mNAP, and B_bk_jF were the most abundant PAHs in the non-heating seasons, while FLT, PYR and also B_bk_jF were found as the most detectable compounds in the heating seasons.

The concentrations of BaP, which is regarded by the WHO and the EEA as a good index for PAH carcinogenicity, ranged from undetected to 8 ng/m³ with the mean value of 1.01 ng/m³

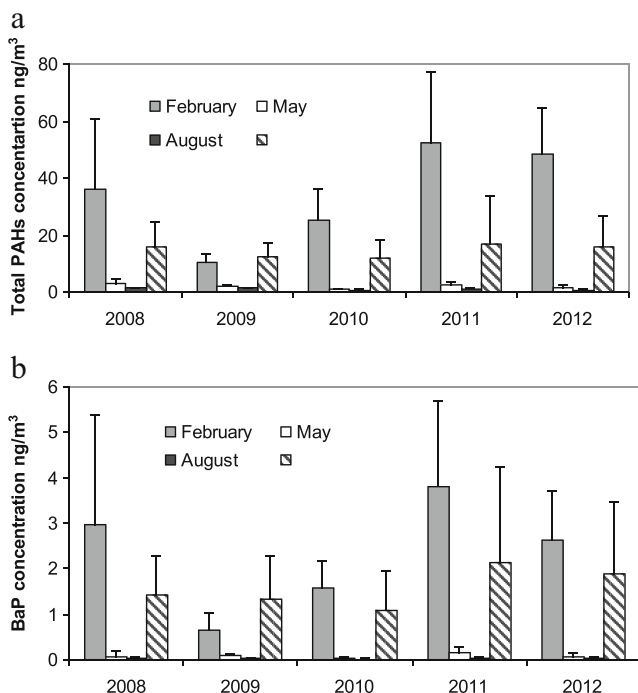


Fig. 3 Temporal variation of total PAHs and BaP concentrations in PM₁₀ in Győr, Hungary (error bars represent one standard deviation)

in the period of 2008–2012 (Table 1). Similar to the concentration trends of total PAHs and PM₁₀, relatively higher BaP levels were detected in samples collected in November and February (Fig. 3b). The BaP concentration exceeded the Hungarian daily limit value of 1 ng/m³ in 61 % of the samples collected in heating seasons. The comparison of the daily BaP concentrations with the daily AQI values show acceptable, polluted or heavily polluted results in heating seasons, while excellent or good air quality was indicated in spring and summer (Table 2). The annual average concentrations of BaP were in the range of 0.53–1.54 ng/m³. This indicates that BaP concentration exceeded the Hungarian annual limit value of 0.12 ng/m³ in all the 5 years, and the study area has heavily polluted air quality according to the Hungarian AQI.

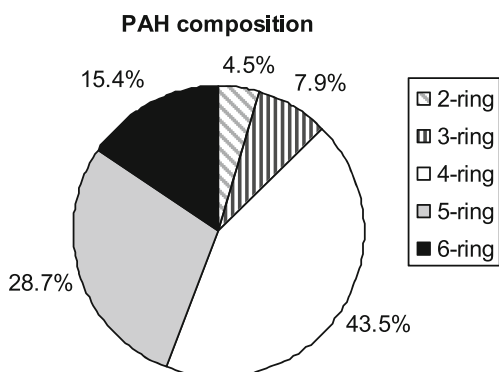


Fig. 4 Compositional pattern of PAHs by total aromatic rings in PM₁₀ in Győr, Hungary

However, the annual average concentrations of BaP for years 2009 and 2010 were below the EU and the equivalent Hungarian target value (1 ng/m³).

It is well known that BaP is easily degraded in the presence of sunlight and oxidants (Cheng et al. 2007). Due to degradation, BaP concentration alone does not give a good indication of the hazard posed by all the PAHs. The carcinogenic potential of PAHs could be underestimated if this compound alone is taken as the representative of carcinogenicity. For better quantification of aerosol carcinogenicity related to whole PAH fraction, BaP-equivalent carcinogenic potency (BaPE) has been introduced as an index and calculated using the following equation (Cheng et al. 2007; Muránszky et al. 2011):

$$\text{BaPE} = \text{BaA} \times 0.06 + \text{BF} \times 0.07 + \text{BaP} + \text{DahA} \times 0.6 + \text{IND} \times 0.08 \quad (1)$$

wherein BF includes all the isomers of benzo[fluoranthene].

The BaPE index tries to parameterise the health risk for human health related to ambient PAH exposure, and is calculated by multiplying the concentrations of each carcinogenic congener with its carcinogenic factor obtained in laboratory studies. In this study, the BaPE concentrations ranged from undetected to 10.92 ng/m³ (Table 1). BaPE and BaP had shown similar patterns of seasonal distributions (Figs. 3b and 5). The mean BaPE values were 2.77 and 0.09 ng/m³ in the samples collected in heating and non-heating seasons, respectively. Thus, the local population appears to be exposed to significantly higher cancer risk in the heating seasons.

According to the formation mechanisms, PAHs can be classified as pyrogenic or petrogenic PAHs. Normally, petrogenic sources (unburned crude oil and petroleum products such as gasoline, kerosene, diesel, lubricating oil and asphalt) are characterised by the dominance of LMW PAHs, whereas pyrogenic sources (incomplete combustion of diesel/shale/crude oil/coal leads) are characterised with greater contents of

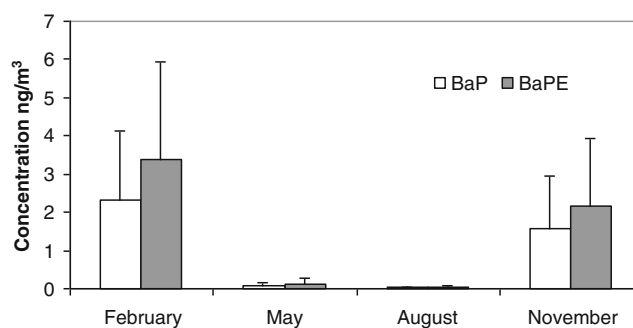


Fig. 5 Levels of BaP and BaP-equivalent in PM₁₀ in Győr, Hungary, at different months based on average concentrations for 5 years (2008–2012) (error bars represent one standard deviation)

MMW and HMW PAHs. It has also been reported that LMW PAHs can be tracers for wood, grass and industrial oil combustion. In contrast, MMW and HMW PAHs are usually associated with coal combustion and vehicular emissions (Khalili et al. 1995). Therefore, ratios between LMW and sum of the MMW and HMW PAHs are used to identify different sources of PAHs. The pyrolytic sources are characterised by a ratio <1 , whereas petrogenic sources show a greater ratio (>1) (Kaur et al. 2013). Comparatively, the ratios between LMW and sum of the MMW and HMW PAHs presented in Table 3 and the high fraction of MMW and HMW PAHs in total PAHs indicate mainly pyrogenic sources in the PM₁₀ samples of Győr. Petrogenic sources were identified only in the non-heating seasons. In addition, some diagnostic ratios of the selected PAHs were calculated for this

study and are listed in Table 3 (Yunker et al. 2002; Ravindra et al. 2008b; Kaur et al. 2013; and references therein). The FLT/(FLT+PYR) ratio reported by Yunker et al. (2002) indicates pyrogenic origins of PAHs (excluding only 3 PM₁₀ samples). Based on concentration ratio of IND/(IND+benzo[ghi]perylene (BghiP)), over 93 % of all our samples show pyrogenic origins with a limited number of samples characterised by PAHs of petrogenic origin. The results of concentration ratios of FLT/(FLT+PYR) and IND/(IND+BghiP) suggest that the combustion of both liquid and solid fuels was the dominant source of PAH contamination. However, the ratio values of BaA/(BaA+CHR) show mixed sources of pyrogenic combustion and petrogenic sources (Yunker et al. 2002). The BaP/BghiP ratio obtained in this study indicate traffic source over 70 % of all the samples. The mean monthly

Table 3 Diagnostic ratios and possible PAH sources in this study

PAH ratio	Possible sources			Ranges and mean values of PAH ratios in this study (2008–2012)			
	Value	Source	Reference	February	May	August	November
LMW/(MMW+HMW)	<1	Pyrogenic	Kaur et al. 2013	0.05–0.25	0.06–1.34	0.16–5.25	0.01–0.47
	>1	Petrogenic		0.14	0.55	1.63	0.13
BaP/BghiP	<0.6	Nontraffic sources	Kaur et al. 2013	0–1.81	0–14.67	0–1.33	0.48–2.44
	>0.6	Traffic source		1.08	0.92	0.52	1.20
PYR/BaP	~ 10	Diesel engine	Ravindra et al. 2008b	0–15.33	0–29.50	0–7.0	0.18–2.79
	~ 1	Gasoline engine		2.17	4.47	1.93	0.93
BaP/(BaP+CHR)	0.07–0.24	Coal combustion	Kaur et al. 2013	0–0.61	0–0.67	0–1.0	0.22–0.68
	0.49	Gasoline		0.39	0.36	0.43	0.52
	0.73	Diesel engine					
	0.5	Diesel	Ravindra et al. 2008b				
	0.7	Gasoline					
FLT/(FLT+PYR)	<0.4	Petrogenic	Yunker et al. 2002	0.46–0.60	0.36–0.73	0.43–0.63	0.16–0.57
	0.4–0.5	Fossil fuel combustion		0.54	0.53	0.53	0.48
	>0.5	Grass, wood, coal combustion					
	1–1.4	Coal combustion	Kaur et al. 2013				
BaA/(BaA+CHR)	<1	Gasoline, diesel engine					
	<0.2	Petrogenic	Yunker et al. 2002	0.21–0.61	0–0.63	0–1.0	0.20–0.60
	0.2–0.5	Petrogenic or combustion		0.46	0.37	0.32	0.45
	>0.5	Combustion					
	0.53	Vehicle emission	Kaur et al. 2013				
	0.73	Diesel engine					
IND/(IND+BghiP)	0.79	Wood burning					
	<0.2	Petrogenic	Yunker et al. 2002	0.46–0.67	0–0.92	0–0.58	0.40–0.65
	0.2–0.5	Petroleum combustion		0.56	0.39	0.42	0.55
	>0.5	Grass, wood, coal combustion					
	0.4	Gasoline	Kaur et al. 2013				
	0.3–0.7	Diesel engine					
	0.35–0.7	Diesel engine	Ravindra et al. 2008b				
	0.56	Coal					
0.62	Wood burning						

BaP/BghiP ratios were higher in heating season. Vehicular emissions can be derived from both gasoline and diesel engines in the Győr atmosphere based on ratios of PYR/BaP, BaP/(BaP+CHR), FLT/(FLT+PYR) and IND/(IND+BghiP) characterised in Table 3 (Ravindra et al. 2008b; Kaur et al. 2013; and references therein). Overall, the pyrogenic origins were the predominant sources of PAH compounds in the PM₁₀ samples of Győr.

Although molecular ratios are often used for characterising possible pollution sources, these ratios are only semi-quantitative. Furthermore, these ratios can be altered due to the reactivity of some PAH species with other atmospheric species, such as ozone and/or oxides of nitrogen. In addition to the atmospheric reactivity, degradation that may occur during the sampling process can also modify the atmospheric PAH levels and thus the ratios between PAHs (Ravindra et al. 2008b).

Concentration of PM₁₀-bound heavy metals

The levels of measured heavy metals at the monitoring station of Győr in the period of 2008–2012 are summarised in Table 1. The mean metallic concentrations calculated for the 5-year sampling period were found in decreasing order of Pb (14.47 ng/m³), Ni (3.73 ng/m³), As (0.64 ng/m³) and Cd (0.60 ng/m³). The four metals typically accounted for about 0.06 % of the total mass of the PM₁₀ fraction in the Győr atmosphere. The monthly average concentrations and standard deviations based on data for the 5-year period are shown in Fig. 6.

The Pb concentrations ranged from 0.19 to 65.98 ng/m³ in the study period. Relatively higher Pb concentrations were found in February and May compared to August and November (Fig. 6a). However, the maximum Pb concentration was 7.8 and 4.6 times less than the EU and the stricter Hungarian annual limit values of 500 and 300 ng/m³, respectively (Table 2). The annual average concentrations were <7 % of the Hungarian limit value.

The Ni concentrations were in the range of 0.19–19.53 ng/m³. The monthly average Ni concentrations and standard deviations illustrated in Fig. 6a show that seasonal variation is not observed. The annual average concentrations were <22 and 18 % of the EU target and the Hungarian limit values (20 and 25 ng/m³), respectively. However, the previous study on air quality of Győr carried out within the ESCAPE project has highlighted that the annual average Ni concentration was above the EU limit value of 20 ng/m³ at 19 sampling sites (Vaskövi et al. 2014). Ni content of PM₁₀ samples collected at the 20 different sampling sites was measured by energy dispersive X-ray fluorescence technique. More than half of the annual average Ni concentrations determined at different sites were in the range of 100–490 ng/m³. The maximum annual average level (1150 ng/m³) determined at a traffic-related site was 58 times higher than the annual EU limit value. Comparison of these results with our Ni concentrations

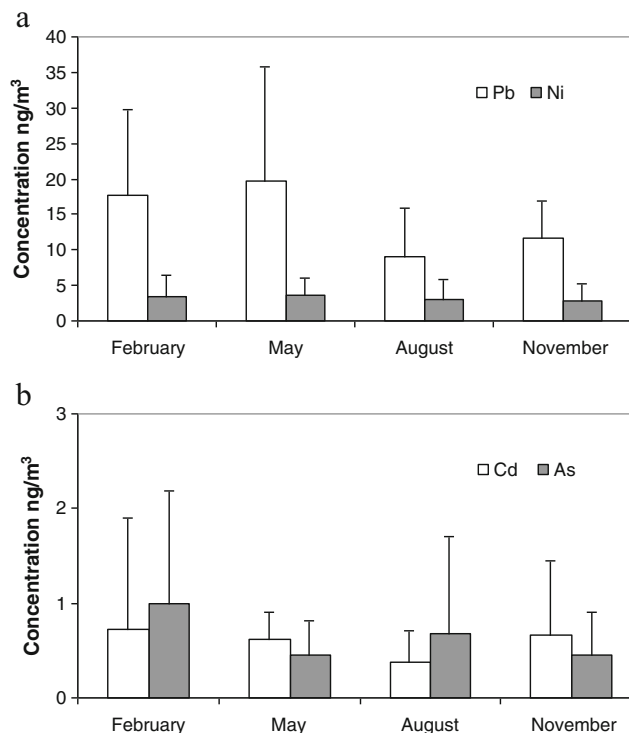


Fig. 6 Heavy metal levels in PM₁₀ in Győr, Hungary, at different months based on average concentrations for 5 years (2008–2012) (error bars represent one standard deviation)

and some published data of polluted Asian urban areas (e.g. Beijing, China, 40±30 ng/m³ in summer, 110±110 ng/m³ in winter (Sun et al. 2004); Taj Mahal, Agra, India, 50±30 ng/m³ (Singh and Sharma 2012); Seoul, Korea, 46±87 ng/m³ (Kim et al. 2002)) or ambient air near the Canadian copper smelters and refineries and zinc plants (5–151 ng/m³ (Newhook et al. 2003)) demonstrates that the ESCAPE results for Ni seem to be incorrect. Thus, measurement or calculation errors can be presumed.

The As concentrations ranged from undetected to 6.64 ng/m³. The annual average concentrations of As were <19 and 12 % of the EU target and the Hungarian limit values (6 and 10 ng/m³), respectively. The Cd concentrations were in the range of 0.03–9.51 ng/m³. The annual average concentrations of Cd were <22 % of the EU target and the equivalent Hungarian limit value (5 ng/m³). Very little seasonal variation is observed in As and Ni concentrations (Fig. 6b).

Overall, the annual average concentrations of each heavy metal (Pb, Cd, As and Ni) observed in our study were below the EU and the Hungarian permitted levels. The AQI results show that the study area of Győr has excellent air quality with respect to metals.

Comparison with other cities in Hungary

Comparative levels of the annual average concentrations of PM₁₀, PM₁₀-bound carcinogenic PAHs (BaP, BaA, BbjkF,

IND and DahA) and heavy metals in some Hungarian urban areas determined under the National PM₁₀ Monitoring Programme in the period of 2008–2012 are summarised in Table 4 (HMS 2009, 2010, 2011, 2012, 2013). Furthermore, Table 4 includes concentration data for the Hungarian background air at K-pusztá located on the Hungarian Great Plain in the middle of the Carpathian Basin (Fig. 1). K-pusztá is as free from direct pollution as possible in the highly industrialised, densely populated central Europe. The nearest big city is the dominantly agricultural Kecskemét.

Based on annual average concentrations compared to the Hungarian AQI values, the air quality for PM₁₀ in the different Hungarian cities was good, acceptable or polluted in the period of 2008–2012. The annual average concentrations of PM₁₀ determined at K-pusztá show good and acceptable air quality. Similar to the results of Győr, the highest annual average values listed in Table 4 were measured in 2011. The PM₁₀ air quality in Hungary generally corresponds to the EU average (EEA 2013). The results based on the EEA database indicate high levels of particulate air pollution in Central and Eastern Europe with large changes between seasons, likely caused by local heating. In a previous study, the effects of emission, long-range transport and meteorological conditions on PM₁₀ concentration in Budapest were analysed for the period of 2006–2010 (Ferenczi 2013). It has highlighted that the reasons of PM₁₀ formation related to air pollution episodes in winter are the unfavourable weather conditions and increased emissions from domestic heating. Similar to the results of Győr, high PM₁₀ concentrations were observed very rarely in summer. While the annual variability of the industrial and traffic emissions in Budapest is not significant, the domestic emissions increase in the winter season. Furthermore, on the basis of a chemical transport model calculation, it was found that in annual average the transboundary sources are responsible for the 70–80 % of the PM₁₀ pollution formation in Hungary. Modelling the effect of long-range transport on local PM₁₀ levels in Hungary, a significant spatial variability was observed.

The annual average BaP concentrations in PM₁₀ aerosols of the Hungarian urban areas often exceeded the EU target value of 1 ng/m³. The highest levels are predominantly measured in the northeastern region of Hungary. At the same time, the average BaP levels obtained in Hungary are still lower than that summarised by Staniszewska et al. (2013) for several Polish cities. In Poland, the BaP concentration in PM₁₀ fraction during the heating season was significantly higher (12.1–36.9 ng/m³) than those observed in the non-heating season (0.1–1.5 ng/m³). In addition, Staniszewska et al. (2013) has highlighted that the BaP concentrations in aerosols are clearly dependent on the air temperature and relative humidity. Low temperature and high relative humidity favour high concentration of BaP in aerosols, whereas high level of precipitation usually decreases the BaP concentration in aerosols.

Moreover, wind direction and air masses trajectories play a major role in determining the BaP concentrations during the heating season. It should also be noted that the summary report on air quality in Europe (EEA 2013) has presented that many stations are approaching and exceeding the target value for BaP for rural, urban, traffic and other (including industrial) station types. The increase in BaP emissions and concentrations in Europe over the past years is therefore a matter of concern, as it is aggravating the exposure of the European population to BaP, especially in urban areas. The main emission sector is the commercial, institutional and household fuel combustion sector, responsible for 84 % of the total emissions of BaP in the EU.

BaPE-index calculated for the Hungarian urban areas and K-pusztá based on the average concentrations during the period of 2010–2012 is illustrated in Fig. 7. Concentration data for the carcinogenic PAHs (excluding BaP) were not determined in some cities including Budapest (Table 4). In a previous study on chemical characterisation of PM₁₀ fractions of urban aerosol in Budapest, the BaPE concentrations were in the range of 0.02–1.61 ng/m³ in the period of 2004–2007 (Muránszky et al. 2011). The carcinogenic species (BaP, BaA, Bb_kF, IND and DahA) together contributed 49 % of the mass of the total PAHs measured on average. Similar to the results of Győr determined in our study, relatively higher BaPE concentrations were detected in aerosol samples of Budapest during winter compared with other seasons. However, the mean BaPE concentrations ranged from 1.26 to 5 ng/m³ at the different urban sites of Hungary in the period of 2010–2012. The two highest concentrations determined for Miskolc and Debrecen were 6.3 and 8.3 times higher than those measured at the Hungarian background site, respectively. Thus, the local population in the northeastern region appears to be exposed to significantly higher cancer risk as compared to the population in other areas. This might suggest that the PAH emission levels in these areas are high and/or climatic conditions are not very favourable for PAH dispersion/dilution.

In the previous study reported by Muránszky et al. (2011), the mean concentrations of Pb, Ni and Cd in Budapest were 30.4, 2.70 and 1.15 ng/m³ in the period of 2004–2007, respectively. The PM₁₀ samples were collected at the same monitoring station, which is listed in Table 4. The mean concentrations in Budapest atmosphere were three to four times lower in the period of 2008–2012. Overall, the annual average concentrations of PM₁₀-bound regulated heavy metals (Pb, Cd, As and Ni) at individual urban sites around Hungary are low. The metal levels were well below the EU and the Hungarian limit and target values. Comparison of the annual average concentrations with the AQI values show that all Hungarian cities listed in Table 4 have excellent air quality with respect to regulated heavy metals. In Europe, human exposure to Pb, Cd, As and Ni ambient air concentrations above the limit or

Table 4 Ranges and mean values of the annual average concentrations of PM₁₀, PM₁₀-bound PAHs and heavy metals in Hungarian urban areas as well as in the background site (K-pusztá) determined under the National PM₁₀ Monitoring Programme in the period of 2008–2012

Sites	PAH compounds (ng/m ³)										Heavy metals (ng/m ³)					
	BaP	BaA	BbkjF	IND	DahA	Pb	Cd	As	Ni							
Győr (present study)	27.78–47.43	0.53–1.54	0.50–1.89	1.48–3.86	0.62–1.68	0.08–0.19	9.03–20.09	0.36–1.06	0.20–1.13	2.27–4.33						
Budapest	34.94	1.01	1.16	2.58	1.14	0.14	14.47	0.60	0.64	3.73						
	33.17–45.33	0.59–1.36	–	–	–	–	6.73–13.10	0.09–0.47 ^{b,c}	0.14–1.13 ^c	0.30–1.08 ^{a,c}						
	37.13	0.92	–	–	–	–	9.81	0.26	0.65	0.70						
Miskolc	35.96–44.82	1.16–4.72	2.13–3.25 ^{ab}	4.6–5.86 ^{ab}	1.71–2.49 ^{ab}	0.5–0.99 ^{ab}	21.43–43.70	0.68–1.15	2.19–3.99	0.48–1.79						
	41.11	2.78	2.67	5.33	2.04	0.69	30.02	0.91	2.68	1.13						
Debrecen	30.77–41.12	0.74–4.15	2.58–3.70 ^{ab}	5.99–6.41 ^{ab}	2.72–11.0 ^{ab}	0.52–2.24 ^{ab}	5.73–14.70 ^{b,c,d}	0.76–1.33 ^{b,c,d}	1.0–1.50 ^{b,c,d}	1.30–6.30 ^{b,c,d}						
	34.86	2.95	2.99	6.16	5.59	1.10	10.22	1.05	1.25	3.80						
Nyíregyháza	27.17–45.7	0.5–3.7	1.01–2.79 ^{ab}	2.83–6.49 ^{ab}	1.18–2.98 ^{ab}	0.25–0.52 ^{ab}	4.82–12.40 ^{b,c,d}	0.53–1.04 ^{b,c,d}	1.20–2.37 ^{b,c,d}	1.12–10.1 ^{b,c,d}						
	33.28	1.79	1.67	4.19	1.80	0.35	8.61	0.79	1.79	5.61						
Dunatújváros	27.36–42.43	0.65–1.22	–	–	–	–	5.40–18.50	0.40–1.67	0.21–0.84	0.50–1.86						
	31.68	0.86	–	–	–	–	11.60	0.71	0.50	0.89						
Szombathely	21.64–36.22	0.63–1.12	0.13–1.04 ^{ab}	0.78–2.39 ^{ab}	0.43–1.10 ^{ab}	0.08–0.10 ^{ab}	8.0–15.84	0.25–0.84	0.33–0.92	1.72–3.72						
	29.27	0.93	0.71	1.91	0.76	0.09	12.25	0.41	0.50	2.87						
Esztergom	21.28–49.57	0.80–1.27	0.77–1.05 ^{ab}	2.1–2.63 ^{ab}	0.72–1.1 ^{ab}	0.09–0.13 ^{ab}	7.31–18.53 ^b	0.32–0.70	0.39–1.53 ^b	2.06–4.50 ^b						
	34.05	0.98	0.94	7.09	0.88	0.11	11.71	0.49	0.75	3.10						
Veszprém	29.72–38.38 ^a	1.23–2.79 ^a	–	–	–	–	–	0.70 ^{a,c,d,e}	0.12 ^{a,c,d,e}	0.70 ^{a,c,d,e}						
	34.0	1.73	–	–	–	–	–	–	–	–						
Pécs	38.56–43.50 ^{ab}	1.38–3.12 ^{ab}	–	–	–	–	–	–	–	–						
	41.64	1.97	–	–	–	–	–	–	–	–						
Szeged	32.08–57.63 ^c	0.92–1.77 ^c	1.07–2.15 ^{ab,c}	2.88–7.42 ^{ab,c}	0.81–2.1 ^{ab,c}	0.06–0.55 ^{ab,c}	13.59–15.90 ^{c,d,e}	0.25–0.26 ^{c,d,e}	0.70–1.30 ^{c,d,e}	0.80–0.86 ^{c,d,e}						
	41.0	1.28	1.61	5.15	1.46	0.31	14.75	0.26	1.0	0.83						
Kecskemét	27.16–45.94	1.25–3.20	1.01–1.18 ^a	3.21–13.61 ^a	1.15–2.0 ^a	0.16–0.37 ^a	8.20–13.10	0.06–0.33	0.58–1.62	0.12–0.63						
	37.66	1.59	1.09	7.05	1.41	0.24	10.42	0.22	1.03	0.51						
Békéscsaba	22.30–50.10	0.84 ^{a,c,d,e}	–	–	–	–	4.67–13.98 ^b	0.33–0.82 ^b	0.80–2.55 ^b	1.16–4.70 ^b						
	33.47	–	–	–	–	–	9.66	0.49	1.72	2.32						
K-pusztá (Hungarian background, rural site)	25.9–33.02 ^{a,b}	0.30–0.54 ^{ab}	0.14–0.23 ^{ab}	0.95–1.40 ^{ab}	0.50–0.73 ^{ab}	0.02–0.04 ^{ab}	2.95–6.72 ^{ab}	0.23–0.27 ^{ab,c}	0.61–0.68 ^{ab,c}	0.26–0.53 ^{a,b}						
	29	0.44	0.17	1.16	0.58	0.03	5.28	0.25	0.65	0.43						

(–) not determined

^aNo data in 2008^bNo data in 2009^cNo data in 2010^dNo data in 2011^eNo data in 2012

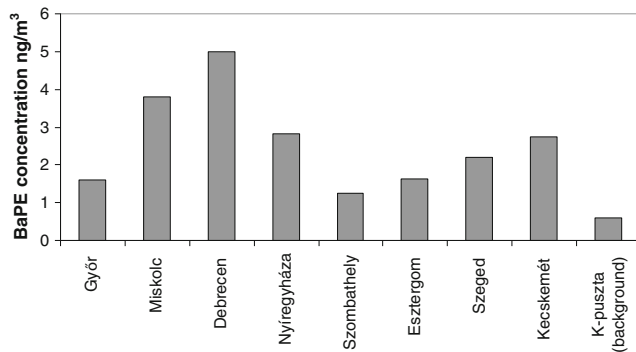


Fig. 7 Mean BaP-equivalent concentration in PM₁₀ at Hungarian urban areas and the background site determined in the period of 2010–2012

target values is a local problem, and is typically caused by specific industrial plants (EEA 2013). Brown et al. (2008) reported the results of 25 years of nationwide ambient metals measurement in the UK. In general, the ambient concentrations of all metals measured by the UK Network, and its predecessors, have decreased steadily during this time. These decreases are the result of a combination of abatement strategies, legislation and changing fuel usage. Similar to our results, the annual average concentrations of Pb, Cd, As and Ni in ambient air are currently well below the EU limit and target values and usually very little seasonal variation was observed in metal concentrations at the sites of UK.

Conclusions

The concentrations of PM₁₀, PM₁₀-bound PAHs (16 US EPA PAHs, mNAP and B_jF) and regulated heavy metals (Pb, Cd, As and Ni) were determined in an urban site of Győr during a 5-year sampling period. Furthermore, the levels of pollutants determined in our study were compared with published data of other Hungarian urban sites. Relatively higher concentrations of both PM₁₀ and PAHs were detected in the Győr PM₁₀ samples collected in the heating seasons compared with spring and summer. However, very little seasonal variation was observed in metal concentrations. Moreover, our study has highlighted that the air quality for PM₁₀ in Hungary generally corresponds to the EU average. It was found that the Hungarian cities have excellent air quality with respect to heavy metals (Pb, Cd, As and Ni). Despite these favourable concentration data, the measurement of ambient heavy metal concentrations is still of great importance for a number of reasons related to human health, the environment and compliance with EU legislation. At the same time, the annual average BaP concentrations at the individual urban sites around Hungary often exceeded the EU target value. The highest BaPE levels are predominantly measured in the northeastern region of Hungary. However, the national air quality database

for carcinogenic PAH species (BaA, B_bk_jF, IND and DahA) at some cities is totally incomplete, which should be supplemented by data. In addition, future air quality studies are needed to characterise and assess the spatial and seasonal variations of PM₁₀-bound PAH concentrations as well as their emission sources, particularly in the northeastern region of Hungary.

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References

- Anderson JO, Thundiyil JG, Stolbach A (2012) Clearing the air: a review of the effects of particulate matter air pollution on human health. *J Med Toxicol* 8(2):166–175. doi:10.1007/s13181-011-0203-1
- Araujo JA (2011) Particulate air pollution, systemic oxidative stress, inflammation, and atherosclerosis. *Air Qual Atmos Health* 4(1):79–93. doi:10.1007/s11869-010-0101-8
- ATSDR (1995) Toxicological profile for polycyclic aromatic hydrocarbons. U.S. Department of Health and Human services, Public Health Service, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta
- ATSDR (2005) Toxicological profile for nickel. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta
- ATSDR (2007a) Toxicological profile for arsenic. U.S. Department of Health and Human services, Public Health Service, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta
- ATSDR (2007b) Toxicological profile for lead. U.S. Department of Health and Human services, Public Health Service, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta
- ATSDR (2008) Draft toxicological profile for cadmium. U.S. Department of Health and Human services, Public Health Service, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta
- Barlow TJ, Boulter PG, McCrae IS, Sivell P, Harrison RM, Carruthers D, Stocker J (2007) Non-exhaust particulate matter emissions from road traffic: a summary report. TRL report for DEFRA, Department for the Environment, Food and Rural Affairs (DEFRA), Scottish Executive, Welsh Assembly Government, and the Department of Environment in Northern Ireland
- Breysee PN, Delfino RJ, Dominici F, Elder ACP, Frampton MW, Froines JR, Geyh AS, Godleski JJ, Gold DR, Hopke PK, Koutrakis P, Li N, Oberdörster G, Pinkerton KE, Samet JM, Utel MJ, Wexler AS (2013) US EPA particulate matter research centers: summary of research results for 2005–2011. *Air Qual Atmos Health* 6(2):333–355. doi:10.1007/s11869-012-0181-8
- Brown RJC, Yardley RE, Muhunthan D, Butterfield DM, Williams M, Woods PT, Brown AS, Goddard SL (2008) Twenty-five years of nationwide ambient metals measurement in the United Kingdom: concentration levels and trends. *Environ Monit Assess* 142(1–3): 127–140. doi:10.1007/s10661-007-9914-9
- Burkart K, Nehls I, Win T, Endlicher W (2013) The carcinogenic risk and variability of particulate-bound polycyclic aromatic hydrocarbons with consideration of meteorological conditions. *Air Qual Atmos Health* 6(1):27–38. doi:10.1007/s11869-011-0135-6

- Cheng J, Yuan T, Wu Q, Zhao W, Xie H, Ma Y, Ma J, Wang W (2007) PM₁₀-bound polycyclic aromatic hydrocarbons (PAHs) and cancer risk estimation in the atmosphere surrounding an industrial area of Shanghai, China. *Water Air Soil Pollut* 183(1–4):437–446. doi:10.1007/s11270-007-9392-2
- EEA (2013) Air quality in Europe—2013 report. European Environment Agency, Luxembourg
- Ferenczi Z (2013) Predictability analysis of the PM_{2.5} and PM₁₀ concentration in Budapest. *Időjárás. Q J Hung Meteorol Serv* 117(4):359–375
- Grahame T, Schlesinger RB (2010) Cardiovascular health and particulate vehicular emissions: a critical evaluation of the evidence. *Air Qual Atmos Health* 3(1):3–27. doi:10.1007/s11869-009-0047-x
- HMS (2009) Summary of the PM₁₀ sampling program in 2008. Hungarian Meteorological Service (HMS), Reference Centre for Air Quality Protection, Budapest, in Hungarian
- HMS (2010) Summary of the PM₁₀ sampling program in 2009. Hungarian Meteorological Service (HMS), Reference Centre for Air Quality Protection, Budapest, in Hungarian
- HMS (2011) Summary of the PM₁₀ sampling program in 2010. Hungarian Meteorological Service (HMS), Reference Centre for Air Quality Protection, Budapest, in Hungarian
- HMS (2012) Summary of the PM₁₀ sampling program in 2011. Hungarian Meteorological Service (HMS), Reference Centre for Air Quality Protection, Budapest, in Hungarian
- HMS (2013) Summary of the PM₁₀ sampling program in 2012. Hungarian Meteorological Service (HMS), Reference Centre for Air Quality Protection, Budapest, in Hungarian
- Hungarian Directive (2011) Guidelines for the air load levels and the stationary point source emissions. 4/2011 (I.14.) VM. Hungarian Ministry of Rural Development, Budapest, in Hungarian
- Kaur S, Senthilkumar K, Verma VK, Kumar B, Kumar S (2013) Preliminary analysis of polycyclic aromatic hydrocarbons in air particles (PM₁₀) in Amritsar, India: Sources, apportionment, and possible risk implications to humans. *Arch Environ Contam Toxicol* 65(3):382–395. doi:10.1007/s00244-013-9912-6
- Khalili NR, Scheff PA, Holsen TM (1995) PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmos Environ* 29(4):533–542. doi:10.1016/1352-2310(94)00275-P
- Kim KH, Mishra VK, Kang CH, Choi KC, Kim YJ, Kim DS, Youn YH, Lee JH (2002) The metallic composition of aerosols at three monitoring sites in Korea during winter 2002. *Environ Monit Assess* 121(1–3):381–399. doi:10.1007/s10661-005-9136-y
- Manoli E, Samara C (1999) Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. *Trends Anal Chem* 18(6):417–428. doi:10.1016/S0165-9936(99)00111-9
- Mehta S, Shin H, Burnett R, North T, Cohen AJ (2013) Ambient particulate air pollution and acute lower respiratory infections: a systematic review and implications for estimating the global burden of disease. *Air Qual Atmos Health* 6(1):69–83. doi:10.1007/s11869-011-0146-3
- MSZ EN 12341:2000 (2000) Air quality. Determination of the PM₁₀ fraction of suspended particulate matter. Reference method and field test procedure to demonstrate reference equivalence of measurement methods. Hungarian Standard Association, Budapest
- MSZ EN 14902:2006 (2006) Ambient air quality. Standard method for the measurement of Pb, Cd, As and Ni in the PM₁₀ fraction of suspended particulate matter. Hungarian Standard Association, Budapest
- MSZ EN 15549:2008 (2008) Air quality. Standard method for measurement of the concentration of benzo[a]pyrene in ambient air. Hungarian Standard Association, Budapest
- Muránszky G, Óvári M, Virág I, Csiba P, Dobai R, Gy Z (2011) Chemical characterization of PM₁₀ fractions of urban aerosol. *Microchem J* 98(1):1–10. doi:10.1016/j.microc.2010.10.002
- Newhook R, Hirtle H, Byrne K, Meek ME (2003) Releases from copper smelters and refineries and zinc plants in Canada: human health exposure and risk characterization. *Sci Total Environ* 301(1–3):23–41. doi:10.1016/S0048-9697(02)00229-2
- Pastuszka JS, Rogula-Kozłowska W, Zajusz-Zubek E (2010) Characterization of PM₁₀ and PM_{2.5} and associated heavy metals at the crossroads and urban background site in Zabrze, Upper Silesia, Poland, during the smog episodes. *Environ Monit Assess* 168(1–4):613–627. doi:10.1007/s10661-009-1138-8
- Ravindra K, Stranger M, Van Grieken R (2008a) Chemical characterization and 3 multivariate analysis of atmospheric PM_{2.5} particles. *J Atmos Chem* 59(3):199–218. doi:10.1007/s10874-008-9102-5
- Ravindra K, Sokhi R, Van Grieken R (2008b) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos Environ* 42(13):2895–2921. doi:10.1016/j.atmosenv.2007.12.010
- Rodríguez S, Querol X, Alastuey A, Rosa J (2007) Atmospheric particulate matter and air quality in the Mediterranean: a review. *Environ Chem Lett* 5:1–7. doi:10.1007/s10311-006-0071-0
- Saraga DE, Maggos TE, Sfetsos A, Tolis EI, Andronopoulos S, Bartzis JG, Vasilakos C (2010) PAHs sources contribution to the air quality of an office environment: experimental results and receptor model (PMF) application. *Air Qual Atmos Health* 3(4):225–234. doi:10.1007/s11869-010-0074-7
- Singh R, Sharma BS (2012) Composition, seasonal variation and sources of PM₁₀ from world heritage site Taj Mahal, Agra. *Environ Monit Assess* 184(1–3):5945–5956. doi:10.1007/s10661-011-2392-0
- Sram RJ, Binkova B, Beskid O, Milcova A, Rossner P, Rossner P Jr, Rossnerova A, Solansky I, Topinka J (2011) Biomarkers of exposure and effect—interpretation in human risk assessment. *Air Qual Atmos Health* 4(3–4):161–167. doi:10.1007/s11869-011-0133-8
- Srogi K (2007) Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. *Environ Chem Lett* 5:169–195. doi:10.1007/s10311-007-0095-0
- Staniszewska M, Graca B, Beldowska M, Saniewska D (2013) Factors controlling benzo(a)pyrene concentration in aerosols in the urbanized coastal zone. A case study: Gdynia, Poland (Southern Baltic Sea). *Environ Sci Pollut Res* 20(6):4154–4163. doi:10.1007/s11356-012-1315-0
- Sun Y, Zhuang G, Wang Y, Han L, Guo J, Dan M, Zhang W, Hao Z (2004) The air-borne particulate pollution in Beijing—concentration, composition, distribution and sources. *Atmos Environ* 38(35):5991–6004. doi:10.1016/j.atmosenv.2004.07.009
- Thorpe A, Harrison RM (2008) Sources and properties of non-exhaust particulate matter from road traffic: a review. *Sci Total Environ* 400(1–3):270–282. doi:10.1016/j.scitotenv.2008.06.007
- Vaskövi B, Udvardy O, Szalkai M, Anda E, Beregszászi T, Nádor G, Varró MJ, Hollósy G, Paller J, Brunekreef B, Beelen R, Meliefste K, Hoek G, Wang M, Eeftens M, Hoogh KD, Rudnai P (2014) Spatial distribution of air pollution in Győr, based on the measurement results of the escape project. *Egészségtudomány (Health Sci)* 18(1):8–33 (in Hungarian)
- WHO (2000) Air quality guidelines for Europe. World Health Organization, Regional Office for Europe, Copenhagen
- WHO (2005) WHO air quality guidelines, global update 2005. World Health Organization; Regional Office for Europe, Copenhagen
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell HR, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33(4):489–515. doi:10.1016/S0146-6380(02)00002-5